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INVESTIGATION OF A POSSIBLE RELATIONSHIP BETWEEN INTERNAL TEARING STRENGTH, TENSILE STRENGTH, FIBER STRENGTH, AND FIBER LENGTH PROPERTIES

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SUMMARY

The balance between tearing strength and tensile strength has been used for many years as a control test for end-use properties of certain paper products, as a tool for pulp evaluation, and as a means for following and distinguishing different types of beating actions. Qualitative information indicates that both fiber length and strength are beneficial to the development of optimum tensile strength and tearing strength combinations. In fact, plots of tearing strength *vs.* tensile strength are sometimes taken as a crude indication of fiber length and/or fiber strength properties, i.e., higher tearing strength at a given tensile strength level appears to be indicative of the presence of longer and/or stronger fibers in the pulp.

Until now, no quantitative basis appeared to exist for these comparisons. A review of the factors involved in tearing and tensile strength, however, suggests that quantitative relationships may be evolved for the experimental variables. There are indications, for example, that experimental interrelationships between tearing strength (T_F), tensile strength (T), weighted average fiber length (F), and fiber strength [zero-span tensile strength (Z)] can be quantitatively described by:

$$T_F = AL^2(1 - T/Z)^2 + CT/Z$$

where A and C are constants for a given pulp over normal ranges of beating and moderate applications of additives.

It is felt that the equation may find practical application in a variety of areas involving the evaluation of pulps, bonding agents, beating equipment, etc. Suitable modifications of the equation may also be adapted for a variety of purposes such as defining beating actions, estimating fiber length changes during beating from tearing and tensile strength properties, or predicting the tearing strength to tensile strength balances that are achieved when a variety of different bonding agents are applied to a specific stock.

The derivation of this particular equation was based on assumptions that are compatible with presently available data. It would be desirable, however, to perform additional experimental work to determine how closely these assumptions actually approach true conditions. Such work would be expected to increase our knowledge of the manner in which stock properties influence paper strength, and materially aid our understanding of the quantitative interrelationships between strength properties.

INTRODUCTION AND REVIEW

UTILITY OF TEARING STRENGTH AND TENSILE STRENGTH MEASUREMENTS

Tensile strength and tearing strength measurements have been used for many years as control tests for end-use properties of paper products, as tools for pulp evaluation purposes, and as a means for following and distinguishing different types of beating actions. It is generally known that all types of paper require certain minimum tensile strength and tearing strength standards,

and that these properties are particularly important in such applications as building papers, bag papers, wrapping papers, printing papers, certain grades of boxboard, saturating papers, etc. In most cases, however, it is impossible to maximize tensile strength and tearing strength in the same paper. This is due to the fact that the beating operations utilized in the preparation of papermaking pulps usually enhances tensile strength at the expense of tearing strength, i.e., tensile strength increases with beating, whereas tearing strength decreases.* Thus, it is generally necessary to establish some mutually beneficial balance between these two inversely related strength factors.

It is also known that the particular balance of tearing strength and tensile strength produced during beating varies with different types of pulps, as well as with their degree of cooking and bleaching. Consequently, these two strength measurements have found extensive use in laboratory beater evaluations of pulps, and they have supplied useful guides for estimating the suitability of particular pulps, cooking processes, etc., for specific paper end-uses. Tensile strength/balances have also been found to vary with different types of mechanical treatments and beating actions. Methods of strength analyses for this purpose have been summarized by Casey (1). It has been found, for example, that the tearing strength properties of a given furnish are a highly satisfactory indication of the amount of fiber length reduction brought about by mechanical

*It should be noted that both tensile strength and tearing strength may simultaneously increase in the very early stages of beating, and that certain short-fibered, low-bonding hardwood pulps may continue to increase in tearing strength over the entire beating cycle. Tearing strength, however, decreases over the major portion of the beating cycle with the more common softwood pulps and moderate fiber length stocks.

refining. Thus, a disproportionately low tearing strength, in comparison with tensile or bursting strength, can be taken as evidence of too much fiber cutting during fiber treatment. Likewise, a very high tearing strength and low tensile or bursting strength may be taken as evidence of insufficient beating, whereas a low tearing strength and high tensile strength generally indicates overbeating.

FACTORS INFLUENCING TENSILE STRENGTH AND TEARING STRENGTH

The importance of tensile and tearing strength to the end uses of paper, control methods, and pulp evaluation techniques has fostered considerable research into the basic fiber properties governing these tests. Results in certain areas of this research are relatively well defined and widely accepted at the present time, whereas other areas remain a source of controversy. In general, however, three primary factors considered important to the development of both tensile and tearing strength are the degree to which the fibers are bonded in the sheet of paper, the strength of the fibers, and their length (2, 3, 4, 5, 6).

Studies of the portion of pulp fibers that actually rupture during tensile strength tests (5), indicate that relatively few fibers fail in lightly bonded sheets developed at low levels of beating. Fiber failure, however, progressively increases with the degree of beating and the extent of interfiber bonding, until large portions of the fibers are ruptured during the test. This suggests that interfiber bonding may be the primary factor limiting tensile strength at the lower levels of bonding, but that fiber strength, as well as interfiber bonding, becomes important at moderate and high levels of bonding. Thus, it may be expected that the ultimate tensile strength development

of a pulp will be achieved when interfiber bonding is high enough to cause all of the fibers to rupture in the zone of tensile failure. In this case, the limiting factor in the tensile strength of the paper would be the strength of the individual pulp fibers. In actual papermaking practices, interfiber bonding is rarely, if ever, developed to the point where such ultimate tensile strength levels are realized. It is possible, however, to obtain an indication of these maximum strengths by means of zero-span tensile strength tests. In this test, a specimen of paper is gripped with the two test jaws set just as close as fine machining will permit, so that the fibers in the sheet are gripped and broken when the jaws are separated (5).

The role of fiber length in tensile strength is not clearly understood at present, although it is thought to be associated with the manner in which stresses are distributed within the sheet. Fiber length appears to be considerably more important to the development of tearing strength than to tensile strength, and weighted average fiber length values appear to be a better measure of the contribution of length to various paper strengths than simple average fiber length values (4).

Investigations involving the portion of fibers ruptured during tearing strength tests (5) indicate that the number of fiber failures progressively increase with increases in interfiber bonding and the degree of beating of the pulp. Thus, the phenomena of increased fiber failure with increased bonding appears to follow similar trends in the development of both tearing and tensile strength.

It has been theorized (6) that in the process of tearing, a portion of the fibers are ruptured, while the other fibers bridging the zone of failure

are pulled intact from one or the other side of the test specimen bordering the failure. Thus, tearing strength, which is actually a work function, may be considered to be the sum of the work required to rupture that portion of the fibers that fail along the line of tear, plus the work required to free those fibers that are pulled free from the fibrous network during the test.

It has been further postulated that considerably more work may be required to free a fiber from the sheet during the tear test than to rupture it. This is because of the importance of the distance term in the force times distance product that constitutes work. Rupture of a fiber requires a substantial force, but it acts over only a very short distance. Consequently, the work involved is small. Less force may be required to pull the intact fiber from the sheet, but the force acts over a considerable distance (the length of the freed fiber segment) and hence, considerable work is involved.

In the earlier stages of beating, interfiber bonding is low and most of the fibers are pulled from the sheet during tearing. This requires a relatively large amount of work and tearing strength values are high. As beating and bonding increase, the force required to pull the fibers from the sheet increases and tearing strength goes up. In most cases, however, a point is reached where increased bonding firmly fixes a portion of the fibers in the sheet, and they rupture rather than pull free. This reduces the work required to tear the sheet and results in lower tearing strengths. The portion of fibers ruptured then steadily increases with increased bonding and tearing strength progressively decreases. Thus, very low tearing strengths might be expected at a point where bonding is sufficient to cause all of the fibers to rupture during the tearing test.

The beneficial influence of fiber length on tearing strength can be readily seen by considering its influence on the work involved in pulling fibers free from the sheet, i.e., an increase in fiber length increases the distance term in the work function and, hence, increases tearing strength. Extremely low tearing values might be expected if the fibers are reduced to very short lengths during beating. Fiber strength might also be expected to play an important role in tearing strength, i.e., stronger fibers will tend to resist rupture at higher levels of interfiber bonding and, consequently, allow an increase in the force and work necessary to pull the intact fibers from the sheet.

To date, most of the major efforts to quantitatively relate pulp or fiber properties to sheet strengths have been limited to attempts to understand the factors involved in single strength properties. Once these factors are thoroughly understood it will be possible to examine the specific fiber characteristics that are important to different sheet strength interrelationships, and it will be possible to determine what fiber properties should be accentuated for the development of beneficial combinations of sheet strengths, i.e., combinations of both high tearing strength and high tensile strength, etc. In the meantime qualitative information indicates that both fiber length and strength are beneficial to the development of optimum tensile strength and tearing strength combinations. In fact, plots of tearing strength vs. tensile strength are sometimes taken as a crude indication of fiber length and/or strength properties, i.e., higher tearing strength at a given tensile level appears to be indicative of the presence of longer and/or stronger fibers in the pulp. However, no suitable quantitative interrelationship exists for such comparisons. The present work explores the possibility of quantitatively interrelating these factors.

DEVELOPMENT OF A POSSIBLE QUANTITATIVE RELATIONSHIP

The previous review and discussion suggests several relationships which may provide the basis for a quantitative, or semiquantitative treatment of tearing strength, tensile strength, fiber length, and fiber strength data. Possible interrelationships between these various factors may be developed in the following stepwise fashion:

1. For any given pulp, the number of fibers involved in the zone of tear failure in a given basis weight sheet, would be expected to remain essentially constant over normal ranges of beating and/or with the application of moderate quantities of bonding agents, etc. The number of fibers in the over-all sheet may increase because of fiber cutting during the beating operation, but the actual number of fibers crossing any given line of potential tear failure would remain about the same.

2. It is reasonable to assume that the number of fibers pulled intact from the sheet during tearing decreases, and the number of fibers ruptured increases, with the degree of beating and the extent of fiber compaction and bonding within the sheet. If the number of fibers involved in the zone of failure is designated by n, the number of fibers ruptured at a given degree of beating may be expressed as:

$$n_R = n(N_R) \qquad (1)$$

where:

n_R = the number of fibers ruptured

N_R = the portion of fibers ruptured (ratio of ruptured fibers to total fibers involved in the tear failure)

Likewise, the number of fibers pulled free during tearing may be denoted by:

$$n_p = n(1 - N_R) \qquad (2)$$

where

n_p = the number of fibers pulled free.

3. The work involved in tearing may be considered to consist of two terms. The first term involves the work required to free those fibers which remain intact and are pulled free from the fibrous network of the sheet during the tearing test. The second term consists of the work required to rupture that portion of the fibers that remain in place and fail during the test.

4. Tearing strength, evaluated by the standard internal tearing resistance test (7) and frequently expressed as tear factor, may be taken as a relative indication of the total work involved in both of the work terms. By using tear factor in this manner, it is possible to write the following expression:

$$T_F = W_p + W_R \qquad (3)$$

where:

T_F = tear factor (an indication of the total work involved in the standard tearing resistance test)

W_p = the work involved in pulling free that portion of fibers that are pulled intact from the fibrous network of the sheet during tearing.

W_R = the work involved in rupturing that portion of fibers that fail during tearing

5. The work required to pull the fibers free from the sheet (W_p) may be further broken down into the product of the average force required to pull a fiber segment from the sheet, the number of fiber segments pulled from the sheet, and the combined length of the freed segments. Thus,

$$W_p = F_A[n(1 - N_R)]\, L_{TS} \qquad (4)$$

where:

F_A = the average force required to free a fiber segment

$n(1-N_R)$ = the number of fiber segments freed [see Equation (2)]

L_{TS} = the total length of the freed segments

6. The total length of the freed segments is equivalent to the average length of a segment multiplied by the number of segments, or--

$$L_{TS} = L_{AS}[n(1 - N_R)] \qquad (5)$$

where

L_{AS} = the average length of a freed segment.

7. If the average length of the fiber segments pulled free during the tearing test is assumed to be directly proportional to the average fiber length of the stock, it is possible to express the average length of a freed segment by:

$$L_{AS} = kL \qquad (6)$$

where

k = the proportionality constant

$\mathbb{L}$ = the average fiber length of the stock

8. Substitution of (kL) for (L_{AS}) in Equation (5) results in:

$$L_{TS} = kL[n(1 - N_R)] \qquad (7)$$

Substitution of $kL[n(1 - N_R)]$ for L_{TS} in Equation (4) then results in:

$$W_p = F_A kLn^2(1 - N_R)^2 \qquad (8)$$

9. The force required to pull a fiber from the sheet depends upon the frictional forces holding the fiber within the sheet (which increase with bonding and sheet compaction) and the length of the enmeshed fiber segment which is subsequently pulled free during the tearing action.

10. If the force required to free a fiber segment exceeds some limiting value (F_L), the fiber will rupture rather than pull from the sheet. The actual level of this value will depend upon the strength of the fibers.

11. Most pulps subjected to conditions of moderate to heavy beating will produce sheets displaying both ruptured and pulled fibers after tearing. In such cases it is likely that the removal of the longer fiber segments require forces that approach the rupture level of the fibers,--i.e., forces equivalent to F_L. The shorter fibers, however, will have shorter segments enmeshed in the sheet and will consequently require proportionately smaller forces for their removal. Thus, the average force required to remove a fiber segment may be approximated by:

$$F_A = F_L \frac{L_{AS}}{L_{LS}} \qquad (9)$$

where:

F_A = the average force required to free a fiber segment

F_L = the force required to remove one of the longer fiber segments (F_L is a limiting force beyond which the fiber ruptures).

L_{LS} = the length of a longer fiber segment

L_{AS} = the average length of a freed segment

12. If the average length of the fiber segments pulled free during the tearing test are again assumed to be directly proportional to the average fiber length of the stock, it is possible to rewrite Equation (9) as:

$$F_A = F_L \frac{L}{L_L} \qquad (10)$$

where:

L_L = the length of the longer fibers in the stock

L = the average fiber length of the stock

It may be noted that the use of Equation (10) assumes that the portion of pulled fibers have essentially the same length distribution as the over-all stock.

13. Ordinarily, the fibers in a stock are not materially weakened by typical beating operations. Likewise, the length of the longer fibers present in a stock is usually not drastically reduced by normal beating, although the number of longer fibers in the pulp may be considerably decreased. Thus, in most situations, the F_L and L_L terms in Equation (10) would not be expected to vary much over normal beating ranges and/or under conditions of moderate applications of bonding agents or other additives. The F_L/L_L term in Equation (10) may, therefore, be considered as a constant (P) for any given pulp, and the equation may be rewritten as:

$$F_A = PL \qquad (11)$$

where

$P = F_L/L_L$ (This value may be considered a constant for a given pulp over normal ranges of beating and additive applications)

14. Substitution of PL for F_A in Equation (8), then results in:

$$W_p = Pkn^2L^2(1 - N_R)^2 \qquad (12)$$

It may be noted that terms P, k, and n^2 in Equation (12) have all been considered a constant for a given pulp. Consequently, the over-all work term for fiber segments pulled from the sheet may be shortened to:

$$W_p = AL^2(1 - N_R)^2 \qquad (13)$$

where:

W_p = the work involved in pulling free that portion of fibers that are pulled intact from the fibrous network of the sheet during tearing.

A = a constant (applies to a given pulp over normal ranges of beating and moderate applications of additives)

L = the average fiber length of the stock

N_R = the portion of fibers ruptured (ratio of ruptured fibers to total fibers involved in the tear failure)

15. The work required to rupture that portion of the fibers that remain in place and fail during the tearing test may be expressed by:

$$W_R = CN_R \qquad (14)$$

where:

W_R = the work involved in rupturing that portion of fibers that fail during tearing.

N_R = the portion of fibers ruptured (ratio of ruptured fibers to total fibers involved in the tear failure)

C = the total work that would be required to rupture all the fibers involved in the tearing test

It may be noted that C in Equation (14) remains constant for a given pulp, and that this value is indicative of the tearing strength obtained when bonding is increased to the point where all the fibers rupture.

16. Substitution of Equations (13) and (14) into the over-all expression for work in Equation (3) results in:

$$T_F = AL^2(1 - N_R)^2 + CN_R \qquad (15)$$

where:

T_F = tear factor.

17. Very few measurements have been reported on the relative portion of fibers that fail during tearing strength and tensile strength tests. The limited information that is available (5), however, suggests that the portion of fibers ruptured in both tests increase with increases in interfiber bonding and sheet compaction. Failure of essentially all the fibers might be expected when the tests are conducted on sheets having extremely high levels of bonding and compaction, whereas, none of the fibers would be expected to rupture at extremely low values of bonding. Apparently, then, the portion of fiber failures occurring in both tests would simultaneously increase or decrease between these two extremeswhen sheet bonding and compaction are adjusted to various intermediate values. This suggests that the portion of fibers ruptured during tensile failures might be used to describe the portion of fibers ruptured during tear failures, and that the N_R term in Equation (15) can be replaced by another term (N_{RT}) that represents the portion of fibers that fail during tensile tests. Such substitution changes Equation (15) to:

$$T_F = AL^2(1 - N_{RT})^2 + CN_{RT} \qquad (16)$$

where:

N_{RT} = the portion of fibers ruptured during tensile strength testing (ratio of ruptured fibers to total fibers involved in sheet tensile failure)

18. It is reasonable to assume that the portion of fibers failing in the tensile test will decrease with increases in fiber strength and increase with increased levels of bonding and sheet tensile strength. Thus, the portion of fibers failing could probably be represented by the ratio of sheet tensile strength to fiber strength--i.e.,

$$N_{RT} = \frac{T}{Z} \qquad (17)$$

where:

T = sheet tensile strength

Z = fiber strength (zero-span tensile strength may be used as an indication of this value).

19. Fiber strength would be expected to remain essentially constant over normal ranges of beating and under conditions of moderate applications of bonding agents and other additives. Thus, on the basis of Equation (17), a straight-line relationship might be expected between sheet tensile strength values (T) and the number of fibers ruptured during the tensile test (N_{RT}). Only limited work has been done in this area, but preliminary data published in the literature (5) appear to be in line with such expectations. These results, plotted in Figure 1, pertain to handsheets prepared from a softwood bleached sulfite pulp beaten various periods in a laboratory Valley beater, and processed at different levels of wet pressing, both with and without the addition of

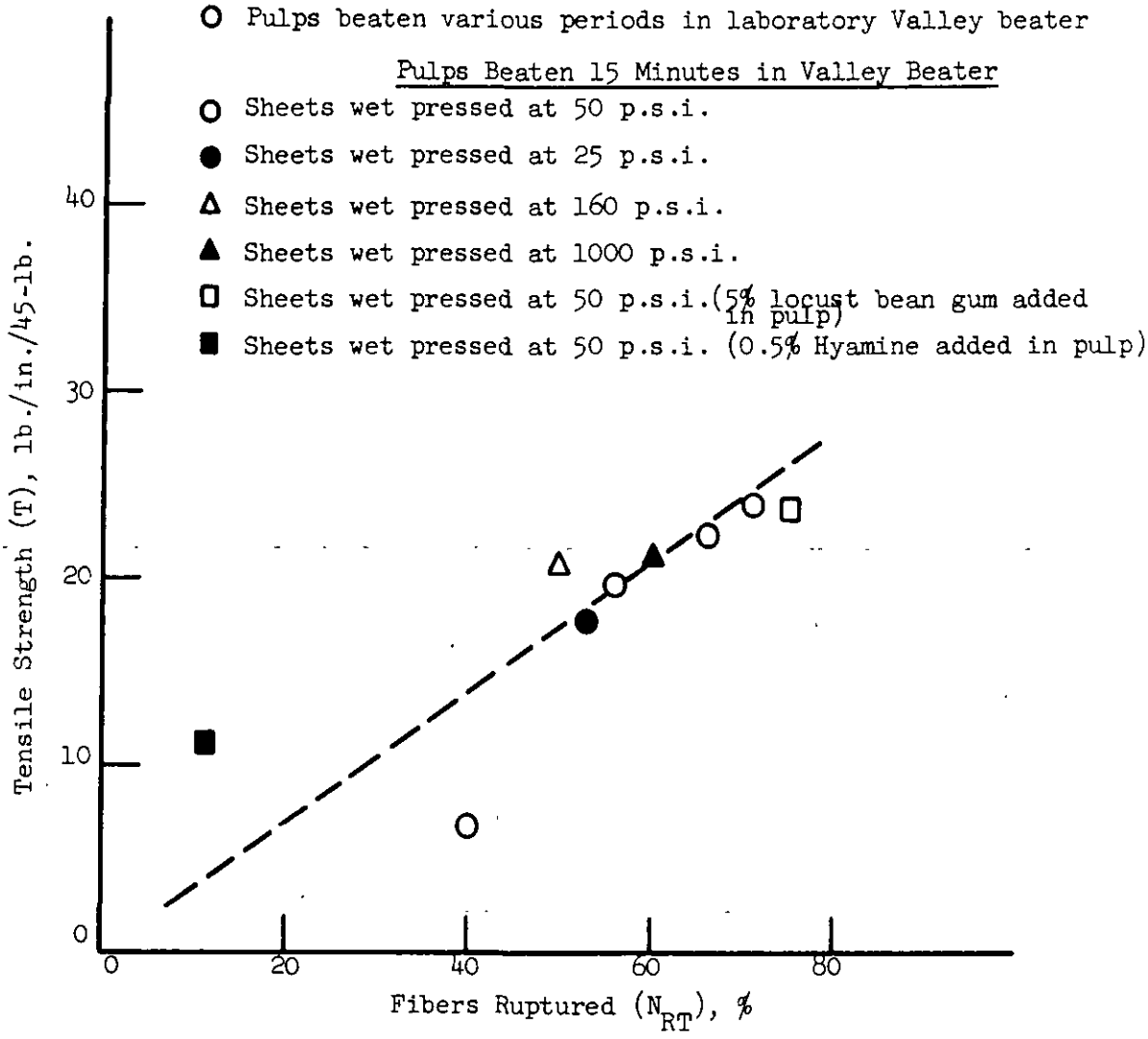

Figure 1. Relationship Between Tensile Strength and the Portion of Fibers Ruptured During Testing

bonding and debonding agents. There is obviously scatter in these results, but there does appear to be a reasonable straight-line relationship, particularly at the moderate and higher levels of beating. Inconsistencies, noted at the lower levels of strength development, may be the result of poor sheet formation and other related effects often experienced in this range of processing.

20. Substitution of T/Z for N_{RT} in Equation (16) results in:

$$T_F = AL^2(1 - T/Z)^2 + CT/Z \qquad (18)$$

21. This expression contains the four experimental variables of sheet tearing strength (T_F), sheet tensile strength (T), fiber length (L), and fiber strength (Z). Suitable values for fiber length properties may be expected from weighted average fiber length determinations. Suitable values for fiber strength might be expected from zero-span tensile strength tests. [Low values are often obtained with this test in the early stages of beating, but they generally level out and reach a plateau after moderate to high levels of processing. It is felt that the best indication of fiber strength may be obtained from the maximum level of zero-span tensile strength obtained over the beating cycle. This value would also be considered the most suitable for use in Equation (18)].

22. The "A" and "C" terms in Equation (18) are constants that pertain to a given pulp over normal ranges of beating and moderate application of additives. The "C" term may be considered an indication of the tearing strength that would be obtained if bonding were great enough to cause all of the fibers to rupture during tear failure.

EXAMINATION OF THE CHARACTERISTICS AND UTILITY OF THE DERIVED RELATIONSHIP

The derivation of Equation (18) was based on assumptions that are compatible with presently available data. However, considerably more experimental work will be necessary before it can be determined how closely these assumptions actually approach true conditions. A large portion of this work would consist of counting the number of fibers ruptured when a variey of different paper sheets are subjected to strength tests. Such efforts would be both tedious and time-consuming, as well as costly. Their application would be justified, however, if they increased our knowledge of the manner in which stock properties influenced paper strengths, and if they materially aided our understanding of the quantitative interrelationships between different strength properties.

It is relatively easy, on the other hand, to obtain data on the tensile strength and tearing strength of sheets, as well as on the fiber length and fiber strength (zero-span tensile strength) properties of pulps. Thus, the effectiveness with which Equation (18) interrelates these four variables may be readily examined under a variety of experimental conditions. If the actual experimental interrelationship between these variables can be satisfactorily described by the equation, it would be a good indication that further work of a more extensive and intensive nature (involving ruptured fiber counts, etc.,) would be warranted. It would also indicate that the equation, in its present form of development, might have utility as a quantitative tool in pulp evaluation work, or for the analysis of different beating characteristics developed by various types of mechanical refiners, etc.

When proceeding with such analysis, however, it might be well to keep in mind two important limitations of the equation. These are:

1. The relationship does not apply at low levels of bonding. It may be recalled that the equation was developed at bonding levels sufficiently high enough to cause some fiber rupture, and at levels where the forces necessary to pull the longer fiber segments from the sheet approached the forces required to rupture the fiber. Thus, certain unbeaten or lightly beaten stocks, may not fit the relationship. This would be particularly true for early portions of the beating cycle where the relative bonding characteristics of some pulps are low enough to cause increases, rather than decreases, in tearing strength with beating.

2. The equation would not be expected to apply if beating were continued to a point where the strength of the fibers were materially reduced. Such decreases in strength, however, are not ordinarily experienced in normal beating cycles.

STRAIGHT LINE PLOTS INDICATED BY THE EQUATION

Dividing both sides of Equation (18) by (T/Z) results in:

$$T_F/(T/Z) = AL^2(1 - T/Z)^2/(T/Z) + C \qquad (19)$$

This modification indicates that a plot of $T_F/(T/Z)$ vs. $L^2(1 - T/Z)^2/(T/Z)$ should result in a straight line having a slope equivalent to A and an intercept equal to C.

Plots of this nature are represented for a variety of different pulps in Figures 2 and 3.* These figures show that tearing strength, tensile strength,

*Complete data for these plots are presented in tables in the appendix.

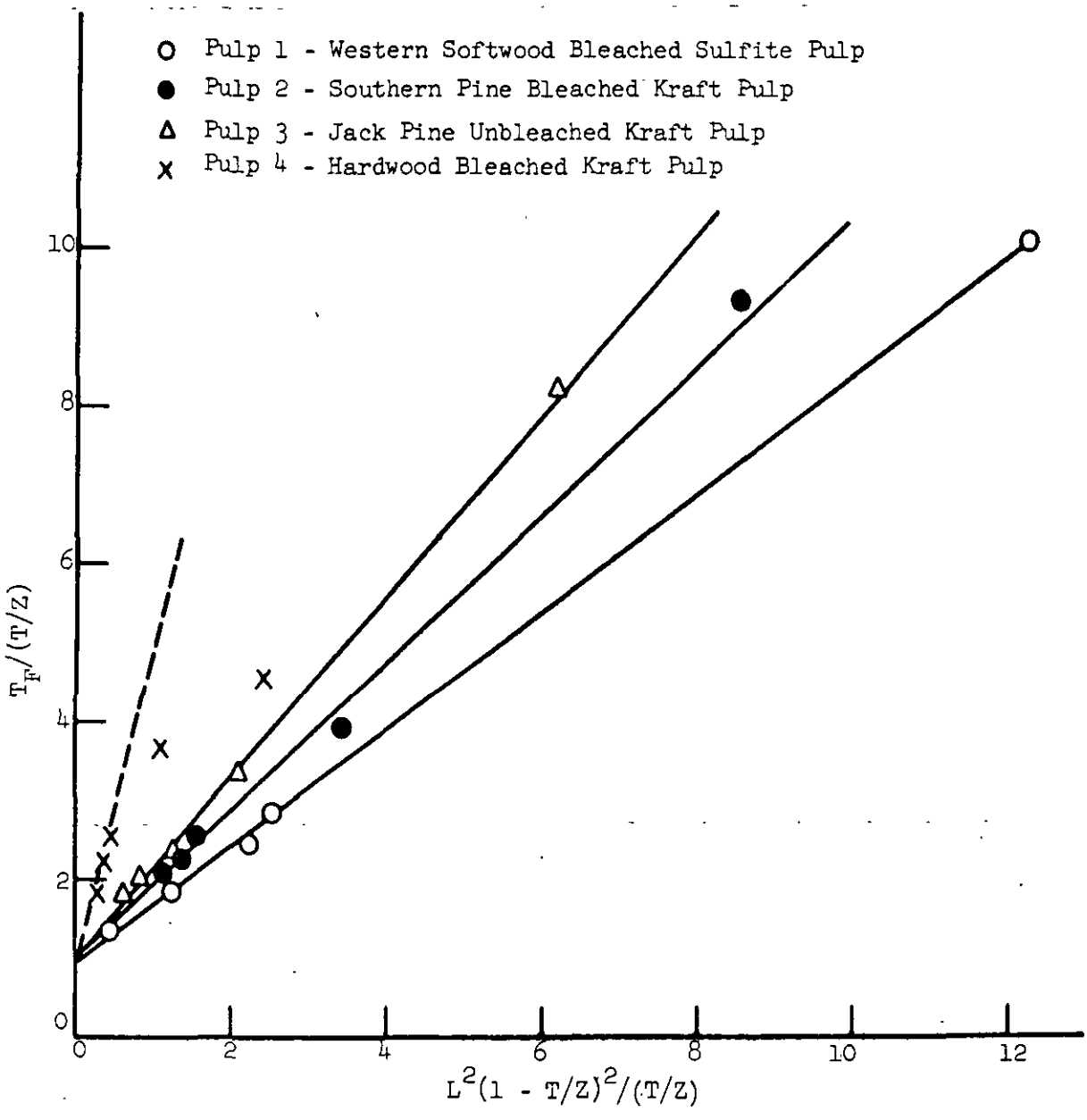

Figure 2. Plots of $T_F/(T/Z)$ vs. $L^2(1 - T/Z)^2/(T/Z)$ for Commercial Pulps Beaten in a Laboratory Valley Beater

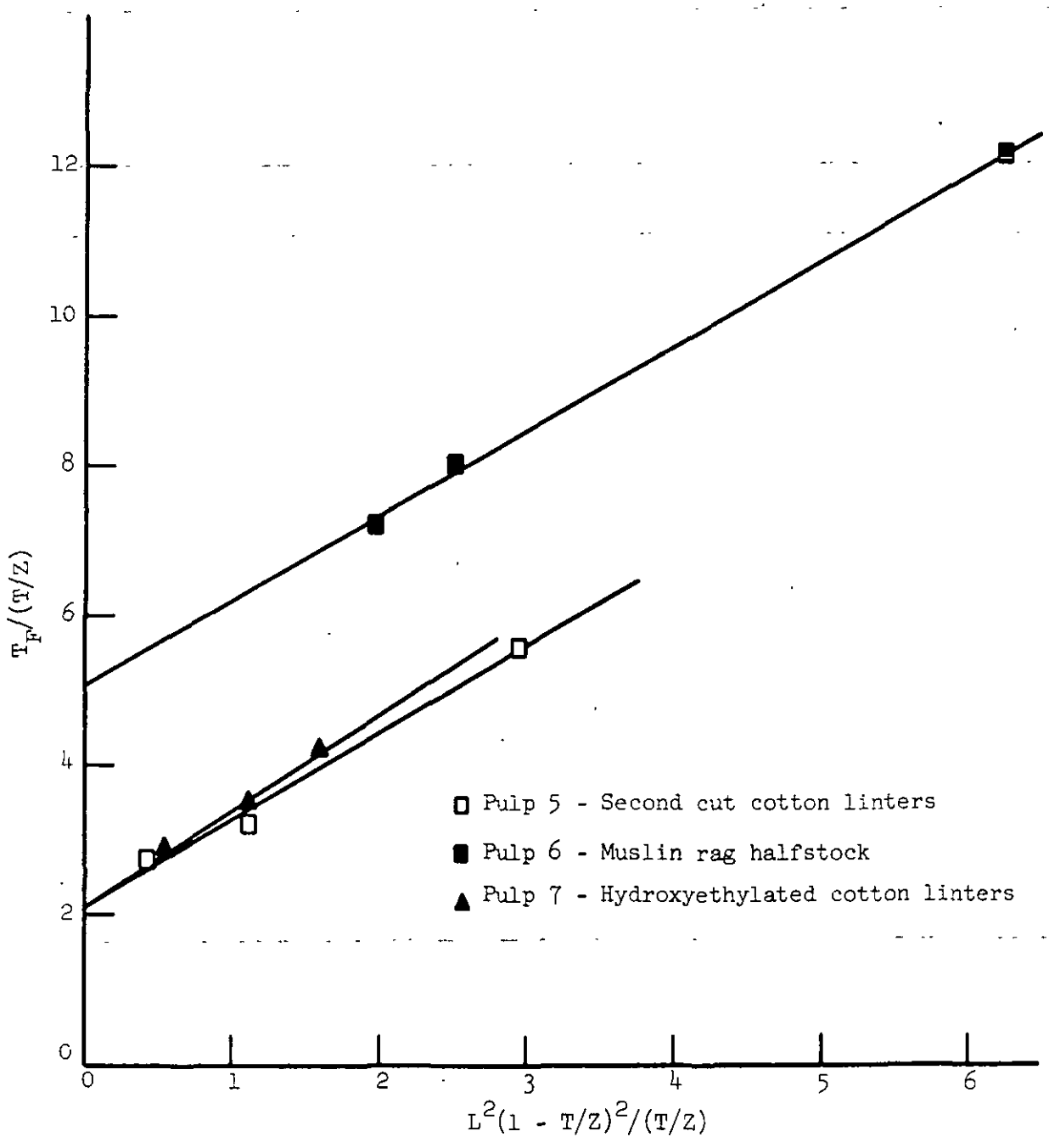

Figure 3. Plots of $T_F/(T/Z)$ vs. $L^2(1 - T/Z)^2/(T/Z)$ for Cotton Pulps Beaten in a Five-pound Noble & Wood Beater

fiber length, and fiber strength (zero-span tensile strength) data obtained over a beating cycle do plot as a straight line when handled in this manner. One exception appears in Figure 2 where two data points for the hardwood pulp obviously do not follow the straight line relationship indicated by the other points. These points, however, would not be expected to fit the relationship because they were obtained at the beginning of the beating cycle where bonding properties were relatively low and tearing strength was actually increasing with increased beating.

The several pulps and the equations relating their tearing strength (T_F), tensile strength (T), fiber length (L), and fiber strength (Z) properties may be summarized as follows:

Pulp 1--Western softwood bleached sulfite pulp
$T_F = 0.750L^2(1 - T/Z)^2 + 0.9\ T/Z$

Pulp 2--Southern pine bleached kraft pulp
$T_F = 0.940L^2(1 - T/Z)^2 + 1.0\ T/Z$

Pulp 3--Jack pine unbleached kraft pulp
$T_F = 1.150\ L^2(1 - T/Z)^2 + 1.0\ T/Z$

Pulp 4--Hardwood bleached kraft pulp
$T_F = 4.0\ L^2\ (1 - T/Z)^2 + 0.8\ T/Z$

Pulp 5--Second cut cotton linters
$T_F = 1.16\ L^2\ (1 - T/Z)^2 + 2.10\ T/Z$

Pulp 6--Muslin rag halfstock
$T_F = 1.14\ L^2(1 - T/z)^2 + 5.05\ T/Z$

Pulp 7--Hydroxyethylated cotton linters
$T_F = 1.29\ L^2\ (1 - T/Z)^2 + 2.10\ T/Z$

Values of T_F calculated from these equations are compared with the actual experimental values in Table I and Figure 4. The good agreement between these values indicate that the experimental interrelationships can be satisfactorily described by the equations and that equations of this nature may have utility in pulp evaluation work and other related applications.

TABLE I

COMPARISON OF EXPERIMENTAL AND CALCULATED TEAR FACTOR VALUES

Pulp	1	2	3	4	5	6	7
Over-all beating range, min.	0 to 39	0 to 55	0 to 70	0 to 50	79 to 162	0 to 110	30 to 151
Beating Interval 1							
Experimental tear factor (T_F)	2.36	2.95	2.61	1.12	1.71	3.94	2.43
Calculated tear factor (T_F)	2.35	2.86	2.55	--[a]	1.69	3.93	--[a]
Beating Interval 2							
Experimental tear factor (T_F)	1.24	1.92	1.73	1.32	1.36	3.24	1.82
Calculated tear factor (T_F)	1.23	2.06	1.75	--[a]	1.43	3.16	1.79
Beating Interval 3							
Experimental tear factor (T_F)	1.12	1.53	1.38	1.21	1.31	3.14	1.64
Calculated tear factor (T_F)	1.18	1.50	1.46	1.22	1.32	3.18	1.66
Beating Interval 4							
Experimental tear factor (T_F)	0.97	1.41	1.29	1.15	--	--	1.50
Calculated tear factor (T_F)	0.95	1.42	1.24	1.13	--	--	1.44
Beating Interval 5							
Experimental tear factor (T_F)	0.82	1.36	1.19	0.97	--	--	--
Calculated tear factor (T_F)	0.74	1.34	1.13	1.03	--	--	--

[a]Bonding was too low for the equation to be utilized in tear factor calculations. In some cases tear factor actually increased with beating in the earlier stages of processing.

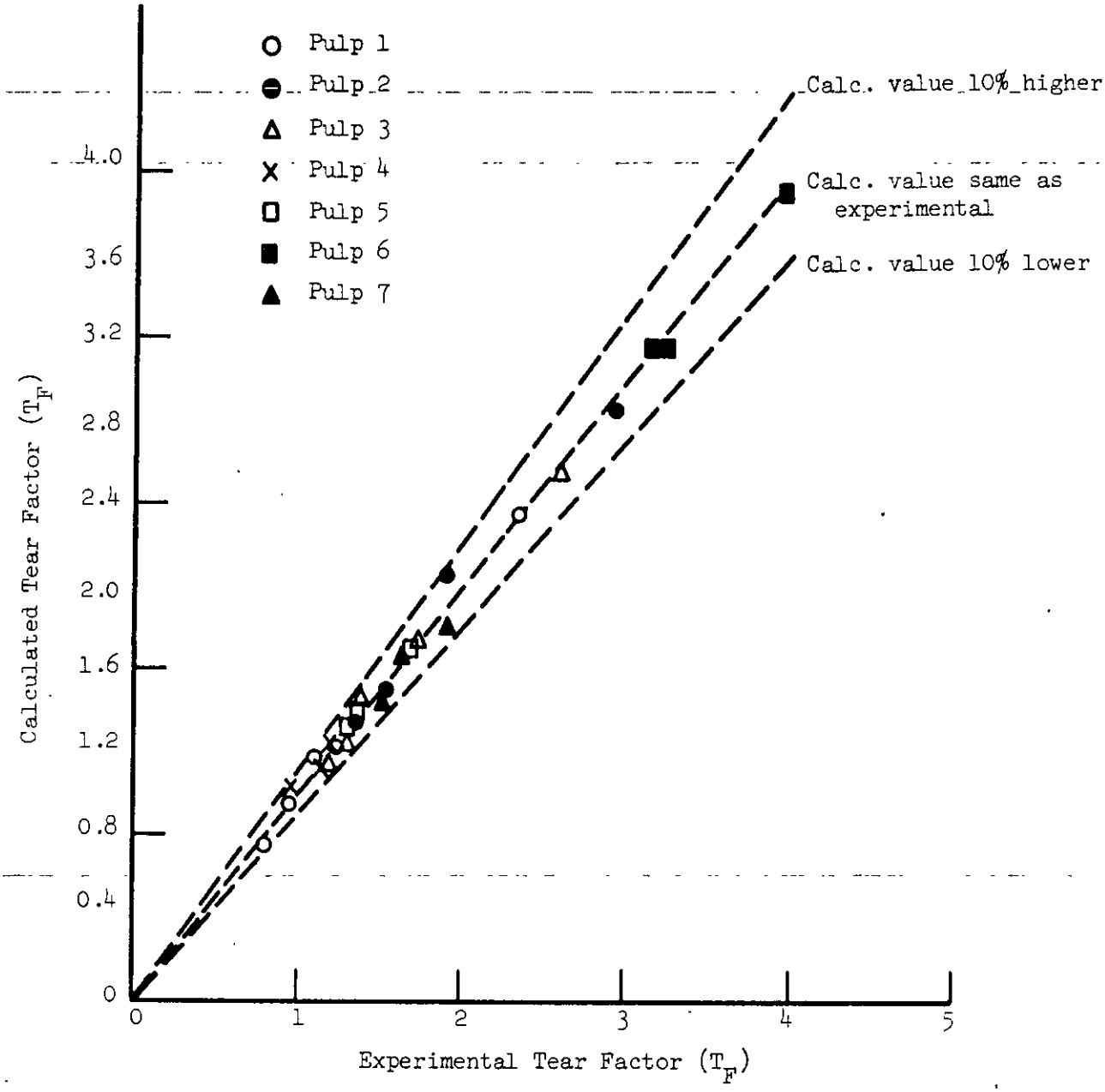

Figure 4. Comparison of Experimental and Calculated Tear Factor Values
Calculated Values Obtained from $T_F = AL^2(1 - T/Z)^2 + CT/Z$

EFFECT OF BONDING AGENTS

Bonding increases, but no changes take place in fiber length when bonding agents are added to a stock. Thus, both the "A" and the "L^2" terms in Equation (18) may be combined into a single constant. Plots of $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$, then would be expected to plot as a straight line having a slope equivalent to "AL^2" and an intercept equal to "C".

Application of bonding agents to the same pulp after additional beating and fiber length reduction would be expected to result in a similar straight line relationship. In this case, however, the slope (AL^2) would be lower (because of the reduced fiber length), although the intercept "C" would be expected to remain the same as that obtained with the longer fibered stock.

Figure 5 shows a plot of $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ values obtained when various applications of locust bean gum were made to a softwood bleached sulfite pulp. Each of the solid lines represent a different level of beating. The arrow indicates the direction of increased gum additions, and the dashed curve shows the relationship developed by processing the pulp over the entire beating cycle without the subsequent addition of any locust bean gum.

If the primary function of a bonding additive is only to improve bonding, it might be expected that the same $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ relationship would be obtained for a given stock, regardless of the type of bonding agent used; i.e., the slope (AL^2) and intercept (C) of the relationship are functions of the stock, and they would not be expected to change unless a different pulp or a stock of a different fiber length were utilized.

Figure 6 shows $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ data obtained when a variety of bonding agents were applied to two cotton linters stocks of different degrees of beating. Applications included 1% methyl-cellulose, 1% locust bean gum, 5% locust bean gum, 1% carboxymethyl cellulose, and 5% carboxymethyl cellulose. The straight line, obtained at each of the two levels of beating, show that the basic relationships between tearing strength and tensile strength are apparently dependent on the properties of the stock and independent of the type of bonding agents applied to the stock. Thus, achievement of a given tensile strength level by the application of bonding agents, would be expected to result in the same tearing strength value, regardless of the different types and amounts of bonding agents that might be utilized. This would be true, however, only when the additives are applied to one given pulp with fixed fiber length characteristics.

Both Figures 5 and 6 further indicate that the equation derived in this work may have utility in describing useful experimental relationships, and predicting tearing strength and tensile strength balances, even in situations where actual fiber length data are not available.

FIBER LENGTH CHARACTERISTICS FROM TEARING STRENGTH AND TENSILE STRENGTH

Figure 7 shows the $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ relationship obtained by beating a Western softwood bleached sulfite pulp. The dashed straight line plots indicate the $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ relationships that would result if bonding agents were added to the pulp at each of the different levels of beating. From previous considerations, it may be seen that the intercept of all of these lines is equal to "C" and their slopes are

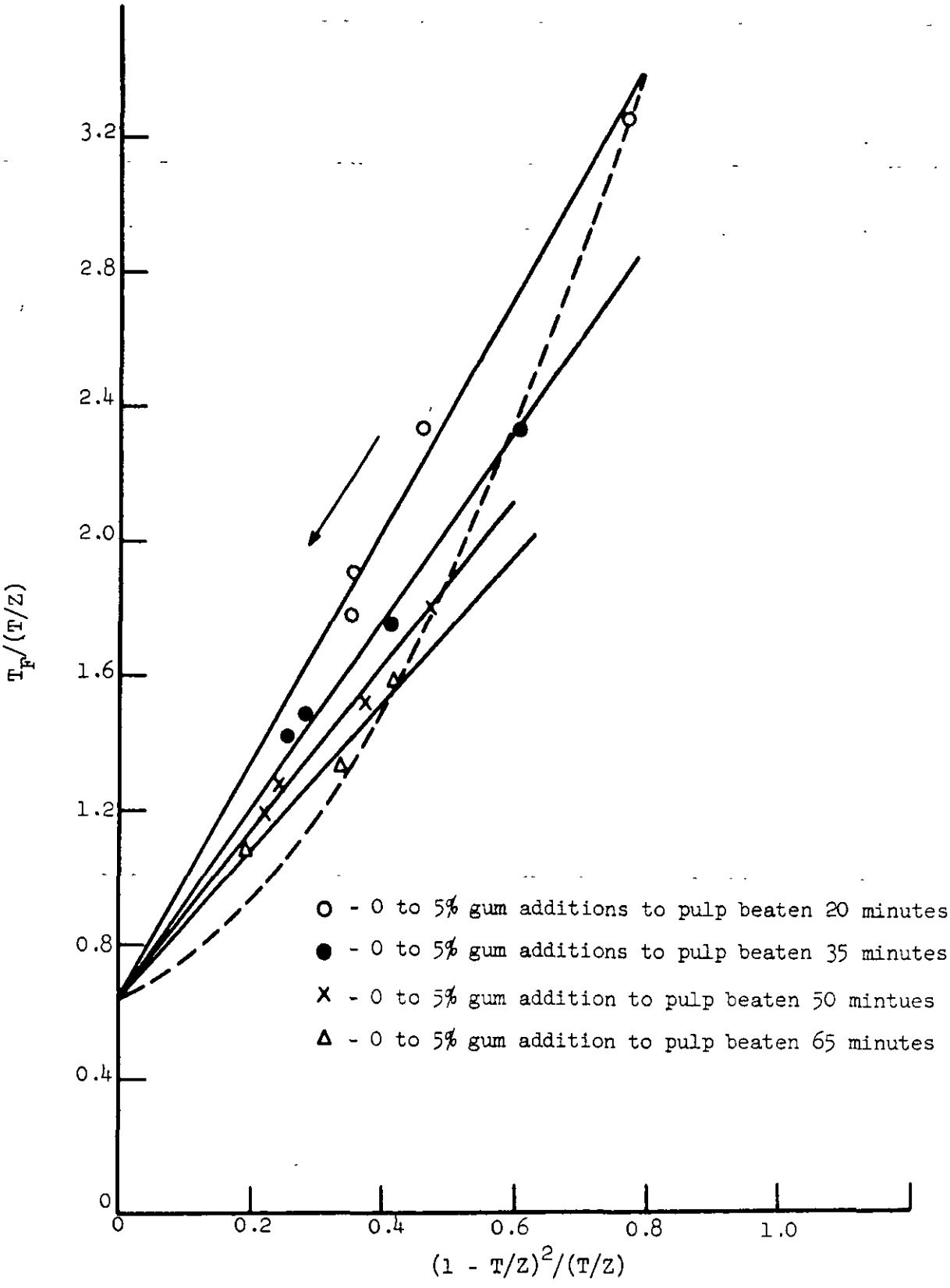

Figure 5. Plots of $T_F/(T/Z)$ vs. $(1-T/Z)^2/(T/Z)$ for Locust Bean Additions to a Bleached Sulfite Pulp

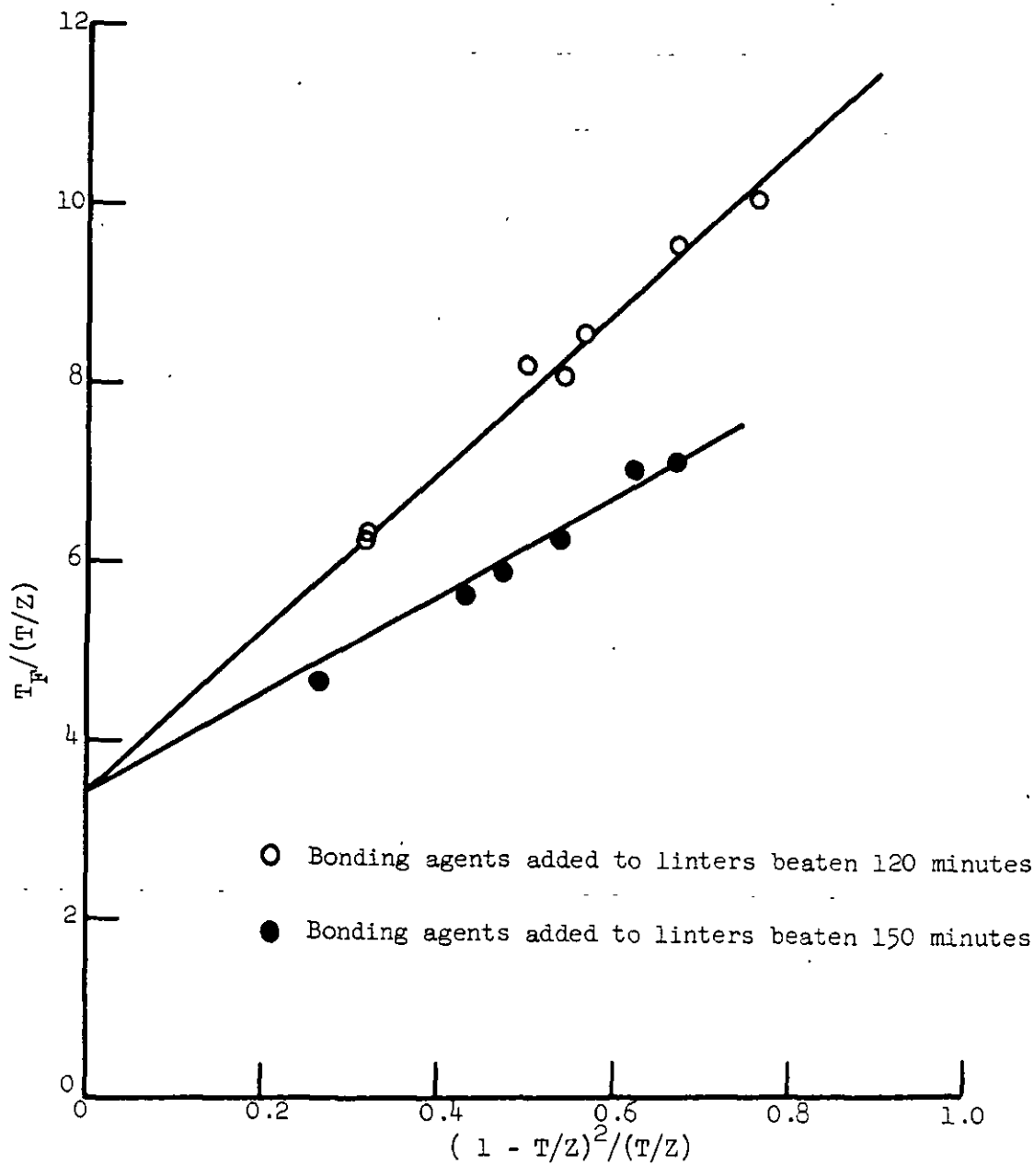

Figure 6. Plots of $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ for Various Additions of Bonding Agents to Cotton Linters

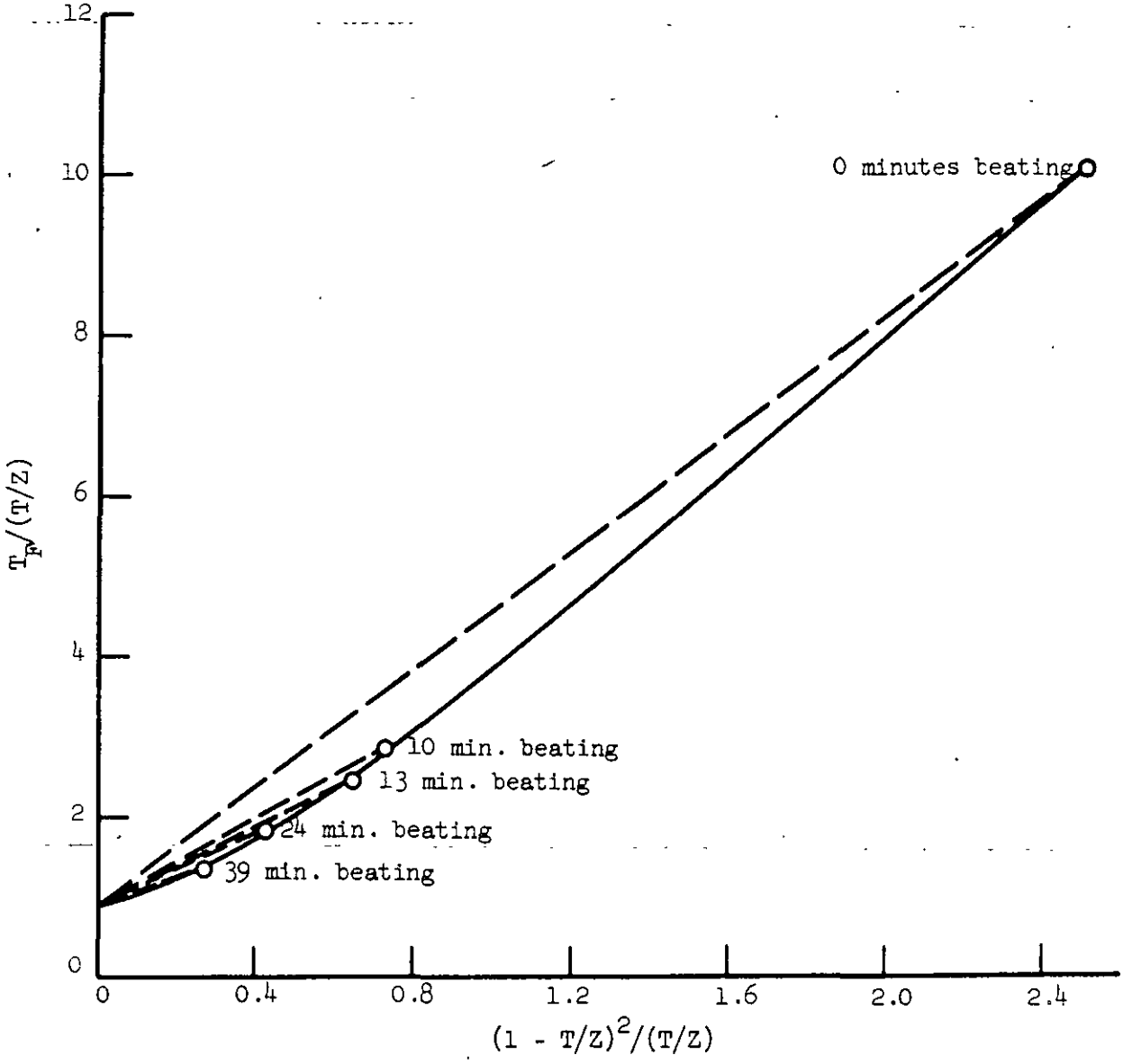

Figure 7. Plot of $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ Relationship Obtained by Beating a Softwood Bleached Sulfite Pulp

equivalent to $\underline{AL}^2$, where "A" is a constant and "L" represents the weighted average fiber length characteristics of the stocks at each of the beating levels. Thus, if L_1 represents the fiber length characteristics after the first beating interval and L_2 represents the fiber length characteristics after the second beating interval, etc., it is possible to write:

$$\sqrt{\frac{S_2}{S_1}} = \sqrt{\frac{AL_2^2}{AL_1^2}} = \frac{L_2}{L_1} \qquad (20)$$

where:

S_1 = the slope of the dashed straight line plot between "C" and the first beating interval

S_2 = the slope of the dashed straight line plot between "C" and the second beating interval

This equation represents the degree of fiber length retention between the first and second beating intervals. In the case of Figure 7, this value is 0.861, indicating that 0.861 or 86.1% of the weighted average fiber length of the pulp at the first level of beating was retained after the second beating interval. Actual fiber length measurements indicate a weighted average fiber length of 2.21 mm. at the first interval (0 minutes beating), and 1.86 mm. after the second beating interval (10 minutes beating). Thus, the experimentally determined retention of weighted average fiber length is 1.86/2.21, which is equal to 0.841 or 84.1%. This value agrees quite well with the 86.1% value calculated from the data plotted in Figure 7. Other comparisons between experimentally determined weighted average fiber length retention values and weighted average fiber length retention values calculated from the slopes of the dashed lines in Figure 7 are summarized as follows:

Beating Interval Range, min.	Weighted Average Fiber Length Retained (Experimental Value), %	Weighted Average Fiber Length Retained (Calculated from Figure 7), %
0 to 10	84.1	86.1
0 to 13	84.1	81.8
0 to 24	77.0	78.8
0 to 39	58.9	67.0

The generally good agreement between the calculated value and experimentally measured values indicate that the equation derived in the work may provide a useful tool for estimating fiber length changes that take place during beating and other mechanical stock preparation treatments.

Such contentions are further supported by Figure 8, where the $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ relationship is plotted for the beating cycle of a Southern pine bleached kraft pulp. The straight line relationship (constant slope) in this case, indicates that "AL^2", and hence, "L" (weighted average fiber length), remains essentially the same over the entire beating cycle. This result is substantiated by fiber length measurements, i.e., measurements indicate a weighted average fiber length of 2.40 mm. at 0 minutes beating, 2.54 mm. at 10 minutes beating, 2.47 mm. after 28 minutes beating, 2.45 mm. at 40 minutes beating, and 2.49 mm. after 55 minutes beating.

Thus, it appears that tearing strength and tensile strength data can supply useful quantitative information on the influence beating, and/or other mechanical treatments, have on fiber length properties.

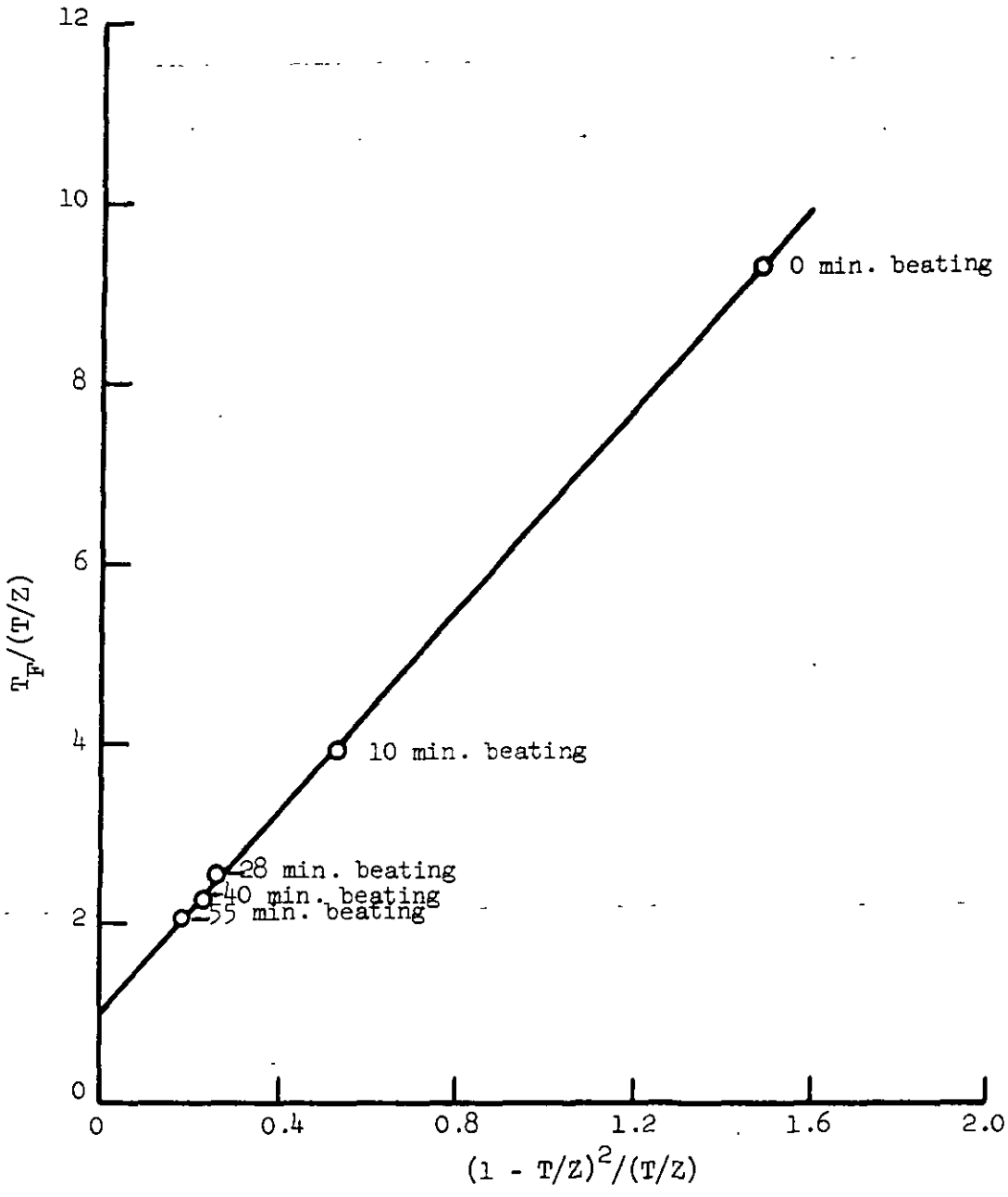

Figure 8. Plots of $T_F/(T/Z)$ vs. $(1 - T/Z)^2/(T/Z)$ Relationship Obtained by Beating a Southern Pine Bleached Kraft Pulp

CONCLUSIONS

The following conclusions may be surmised from the preceding analysis:

1. There are indications that experimental interrelationships between tearing strength (T_F), tensile strength (T), fiber length [weighted average fiber length (L)], and fiber strength [zero-span tensile strength (Z)] can be quantitatively described by the equation derived in this work, i.e., $T_F = AL^2(1 - T/Z)^2 + CT/Z$.

2. The "A" and "C" terms in the equation apparently remain constant for a given pulpover normal ranges of beating and moderate applications of additives.

3. The equation may find practical application in a variety of areas involving the evaluation of pulps, bonding agents, beating equipment, etc.

4. Suitable modifications of the equation may be employed for a variety of purposes such as defining beating actions, estimating fiber length changes during beating from tearing and tensile strength properties, or predicting the tearing strength to tensile strength balances that are achieved when a variety of different bonding agents are applied to a particular stock.

5. The derivation of the equation developed in this work was based on assumptions that are compatible with presently available data. It would be desirable, however, to perform additional experimental work to determine how closely these assumptions actually approach true conditions. Such work would be expected to increase our knowledge of the manner in which stock properties influence paper strength, and materially aid our understanding of the quantitative interrelationships between strength properties.

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APPENDIX

BASIC DATA FOR PLOTS PRESENTED IN THE REPORT

TABLE II

DATA FOR PLOTS IN FIGURES 2, 7 AND 8--COMMERCIAL PULPS BEATEN IN A LABORATORY VALLEY BEATER

Beating Time, min.	Weighted Average Fiber Length, mm.	Tear Factor	Tensile Strength lb./in./45-lb.	T/Z	$T_F/(T/Z)$	$L^2(1 - T/Z)^2$	$L^2(1 - T/Z)^2/(T/Z)$
		Western Softwood Bleached Sulfite Pulp (Highest Zero-Span Tensile = 47.0 lb./in./45-lb.)					
0	2.21	2.36	11.0	0.234	10.08	2.86	12.25
10	1.86	1.24	20.3	0.432	2.87	1.115	2.52
13	1.86	1.12	21.4	0.455	2.44	1.025	2.25
24	1.70	0.97	24.6	0.524	1.85	0.656	1.25
39	1.30	0.82	28.0	0.595	1.38	0.276	0.46
		Southern Pine Bleached Kraft Pulp (Highest Zero-Span Tensile = 49.1 lb./in./45-lb.)					
0	2.40	2.95	15.5	0.316	9.33	2.70	8.53
10	2.54	1.92	24.1	0.490	3.92	1.675	3.42
28	2.47	1.53	29.7	0.605	2.53	0.952	1.57
40	2.45	1.41	30.6	0.622	2.26	0.858	1.38
55	2.49	1.36	32.3	0.657	2.07	0.730	1.11
		Jack Pine Unbleached Kraft Pulp (Highest Zero-Span Tensile = 52.8 lb./in./45-lb.)					
0	2.04	2.61	16.8	0.318	8.21	1.94	6.19
10	2.14	1.73	27.1	0.514	3.37	1.079	2.10
28	2.14	1.38	31.5	0.596	2.32	0.747	1.25
50	2.02	1.29	33.9	0.642	2.01	0.522	0.81
70	1.89	1.19	34.8	0.660	1.80	0.406	0.61
		Hardwood Bleached Kraft Pulp (Highest Zero-Span Tensile = 46.1 lb./in./45-lb.)					
0	1.02	1.12	11.3	0.245	4.56	0.594	2.42
10	0.96	1.32	16.7	0.362	3.64	0.376	1.039
24	0.88	1.21	22.2	0.481	2.52	0.208	0.433
34	0.88	1.15	23.9	0.518	2.22	0.179	0.346
50	0.82	0.97	24.2	0.525	1.85	0.152	0.290

Note: Data were taken from Project Report 6, Project 2210 and 2211 (Feb. 26, 1963). Calculations for tear factor, etc. were based on a basis weight standard of (25 x 40-500).

TABLE III

DATA PLOTTED IN FIGURE 3--COTTON PULPS BEATEN IN A FIVE-POUND NOBLE AND WOOD BEATER

Beating Time min.	Weighted Average Fiber Length, mm.	Tear Factor	Tensile Strength lb./in./45-lb.	T/Z	$T_F/(T/Z)$	$L^2(1 - T/Z)^2$	$L^2(1 - T/Z)^2/(T/Z)$
		Cotton Linters (Highest Zero-Span Tensile = 34.2 lb./in./45-lb.)					
79	1.37	1.71	10.5	0.306	5.59	0.905	2.96
127	1.19	1.36	14.5	0.424	3.21	0.470	1.11
162	0.84	1.31	16.2	0.473	2.77	0.195	0.414
		Muslin Rag Halfstock (Highest Zero-Span Tensile = 49.0 lb./in./45-lb.)					
0	2.10	3.94	15.8	0.323	12.20	2.02	6.25
53.5	1.67	3.24	19.7	0.401	8.06	1.00	2.49
110	1.64	3.14	21.4	0.436	7.20	0.856	1.96
		Hydroxyethylated Cotton Linters (Highest Zero-Span Tensile = 36.2 lb./in./45-lb.)					
30	2.42	2.43	9.4	0.260	9.35	3.21	12.33
90	1.44	1.82	15.7	0.433	4.20	0.684	1.580
120	1.36	1.64	17.0	0.470	3.49	0.520	1.107
251	1.08	1.50	18.7	0.516	2.90	0.274	0.530

Note: Data were taken from Project Report 8, Project 1708 (July 2, 1958). Calculations for tear factor, etc. were originally based on a basis weight standard of (17 x 22-500), but was changed to a standard of (25 x 40-500) for this table. Thus, the data in Tables I and II and Figures 2, 3, and 4 are all on a comparable basis.

TABLE IV

DATA PLOTTED IN FIGURE 5--APPLICATION OF LOCUST BEAN GUM TO SOFTWOOD BLEACHED SULFITE PULP

Gum Applied (Based on Ovendry Pulp), %	Tear Factor	Tensile Strength lb./100-lb./1.5-in.	T/Z	T_F/(T/Z)	$(1 - T/Z)^2/(T/Z)$
		Pulp Beaten 20 Minutes			
0	1.39	0.633	0.426	3.26	0.771
0.5	1.19	0.755	0.509	2.34	0.474
2.0	1.06	0.825	0.555	1.91	0.357
5.0	0.99	0.828	0.557	1.78	0.352
		Pulp Beaten 35 Minutes			
0	1.10	0.695	0.468	2.35	0.605
0.5	0.93	0.788	0.530	1.75	0.416
2.0	0.88	0.876	0.590	1.49	0.285
5.0	0.86	0.902	0.607	1.41	0.254
		Pulp Beaten 50 Minutes			
0	0.92	0.757	0.510	1.80	0.470
0.5	0.83	0.813	0.547	1.52	0.375
2.0	0.79	0.914	0.615	1.28	0.241
5.0	0.75	0.933	0.629	1.19	0.219
		Pulp Beaten 65 Minutes			
0	0.84	0.790	0.531	1.58	0.414
0.5	0.75	0.840	0.565	1.33	0.335
2.0	0.72	0.799	0.537	1.34	0.398
5.0	0.70	0.963	0.649	1.08	0.190

Note: Highest zero-span tensile strength = 1.486 lb./100-lb./1.5-in. Tear factor calculations, etc. based on (25 x 40-500) basis weight standard. Data were taken from Ph.D. Thesis by H. V. Leech: An investigation of the reasons for increase in paper strength when beater adhesives are used. Institute of Paper Chemistry (June, 1953).

TABLE V

DATA PLOTTED IN FIGURE 6--APPLICATION OF VARIOUS BONDING AGENTS TO COTTON LINTERS

Type of Bonding Agent Applied	Agent Applied (based on oven-dry pulp), %	Tear Factor	Tensile Strength lb./in./10 lb.	T/Z	T_F/(T/Z)	$(1 - T/Z)^2/(T/Z)$
		Linters Beaten 120 Minutes				
None	None	4.3	10.1	0.428	10.03	0.765
Methyl Cellulose	1.0	4.1	11.3	0.479	8.56	0.576
Locust Bean Gum	5.0	3.6	13.5	0.572	6.30	0.320
Locust Bean Gum	1.0	3.9	11.4	0.483	8.08	0.554
Carboxymethyl Cellulose (1)	5.0	3.6	13.5	0.572	6.30	0.320
Carboxymethyl Cellulose (1)	1.0	4.3	10.6	0.450	9.55	0.672
Carboxymethyl Cellulose (2)	1.0	4.1	11.8	0.500	8.20	0.500
		Linters Beaten 150 Minutes				
None	None	3.2	10.6	0.450	7.11	0.673
Methyl Cellulose	1.0	3.3	10.9	0.462	7.04	0.625
Locust Bean Gum	5.0	2.8	14.2	0.601	4.65	0.264
Locust Bean Gum	1.0	3.0	12.4	0.525	5.61	0.430
Carboxymethyl Cellulose (1)	5.0	2.8	14.2	0.601	4.65	0.264
Carboxymethyl Cellulose (1)	1.0	3.1	11.5	0.487	6.25	0.540
Carboxymethyl Cellulose (2)	1.0	3.0	12.0	0.509	5.90	0.475

Note: Highest zero-span tensile strength = 23.6 lb./in./10 lb.
Tear factor calculations, etc. were based on a (17 x 22 - 500) basis weight standard.
Data were taken from Project Report 12, Project 1708 (April 10, 1959).

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IRRADIATED GLUCOSE AND CELLULOSE POLYMERS AS BEATER ADHESIVES

INTRODUCTION

During the course of John Snell's thesis program, the observation was made that the high molecular weight water soluble polymer produced by irradiation of glucose was rendered water insoluble by heating in the presence of acid. This gave rise to the possibility that the polymer might function as a wet-strength resin in an acid paper system and exploratory experiments are described herein to test this concept.

From the small quantities of samples left from Mr. Snell's work, two samples were selected for trial of wet-strength properties. One, Sample 125-1, is identified as polymer No. 9 in Mr. Snell's thesis. It was prepared by a 40-megarad irradiation of a glucose solution under a 1.5 Mev. Van de Graaff electron accelerator and has a light scattering molecular weight of approximately 2,000,000. The second, Sample 34-2, is identified as Polymer No. 11 in Mr. Snell's thesis. It resulted from 40 megarad irradiation of a glucose solution under a 8.5 Mev. Linac accelerator and has a light scattering molecular weight of approximately 10,000. The handsheet trials of these materials are described in the following paragraphs.

EXPERIMENTAL WORK WITH GLUCOSE POLYMERS

Preparation of Pulp for Handsheets

Bleached Harmac kraft pulp was beaten to a Schopper-Riegler freeness level of 700 ml. in a 1.5-lb. laboratory Valley beater. This stock was dewatered to about 25% solids, fluffed in a laboratory pulp breaker, and stored at 40°F. The material was subsequently split into 30-g. (oven-dried basis) portions, diluted to a consistency of 1.5%, and dispersed for 5 minutes in a TAPPI standard disintegrator before using in the experimental studies.

Solution of Polymer 125-1

Polymer 125-1 consisted of a 0.2314 g. sample. The material was dissolved in 25-ml. of distilled water in a 50-ml. beaker. This required heating to approximately 70 to 80°C. on a steam bath and the application of 12 drops of 1% sodium hydroxide solution.

Sheet Preparation With Polymer 125-1

The entire 125-1 polymer was added to a 10-g. (O.D. basis) sample of dispersed pulp. This constituted a polymer application level of 2.3% (based on oven-dry fiber). The suspension of pulp and polymer (pH 6.2) was blended for a period of 30 minutes with a small Lightnin' stirrer. At this time 2% rosin (based on oven-dry fiber) was applied, and the stirring continued for another 5 minutes. This was followed by the addition of 4% alum (based on oven-dry fiber), and an additional 5 minutes of blending. The pH at this point was between 4 and 4.5.

The blended slurry was diluted to a consistency of about 0.15% with pH 4 to 4.5 water and formed into TAPPI standard weight handsheets with a TAPPI standard sheet machine. Dilution water in the sheet mold was adjusted to a pH of 4 to 4.5 with dilute hydrochloric acid prior to the addition of the stock slurry. The wet handsheets were pressed between blotters for 5 minutes at 50 p.s.i. and dried on a steam-heated drum drier having a surface temperature of about 240°F.

Solution of Polymer 34-2

Polymer 34-2 consisted of a 1.3771-g. sample. The material was dissolved in 27.5 ml. of distilled water in a 50-ml. beaker. Very little heating and no sodium hydroxide were required.

Sheet Preparation With Polymer 34-2

Handsheets with polymer 34-2 were prepared in the same general manner as those containing polymer 125-1. In this case, however, two 15-g. (O.D. basis) samples of pulp were utilized at polymer applications of 2 and 5%. The pH during the 30-minute blending period of polymer and pulp was 5.4 at the 2% polymer addition level and 4.5 at the 5% level of polymer application. The pH after the addition of alum and during all the subsequent sheetmaking steps was again controlled at 4 to 4.5.

Preparation of Control Handsheets

Control handsheets containing rosin and alum, but no polymer, were prepared in the same general fashion as those containing polymer. Blending periods and pH conditions during sheet formation were similar to those utilized in the work with the polymers.

Handsheet Testing

The handsheets were preconditioned for 60 hours at 29% R.H. and 73°F. and subsequently conditioned and tested at 50% R.H. and 73°F. Evaluation tests included basis weight, caliper, apparent density, tensile strength, stretch, tensile energy absorption, and wet tensile strength after 30-minute and 16-hour soaking periods.

Results

The results of this study are presented in Table I. Apparently, neither of the polymers were very effective in developing wet strength. Sheets prepared with the 125-1 polymer had a noticeable yellowish-tan color indicating that at least some of the irradiated material was retained. Sheets prepared with the 34-2 polymer were also off color, but were not as dark as the 125-1 sheets. This was no doubt due to the fact that the 34-2 polymer itself was somewhat lighter in color than the 125-1 product.

TABLE I

RESULTS OF HANDSHEET TESTS

Preparation of Handsheets				
Type of polymer applied	None	125-1	34-2	34-2
Polymer applied (based on o.d. pulp), %	0	2.3	2	5
Rosin applied (based on o.d. pulp), %	2	2	2	2
Alum applied (based on o.d. pulp), %	4	4	4	4
pH during polymer-pulp blending period	--	6.2	5.4	4.5
pH after alum and during sheet formation	4-4.5	4-4.5	4-4.5	4-4.5
Handsheet Test Results				
Basis weight (25 x 40/500), lb.	47.5	47.0	46.4	47.2
Caliper, mils	5.0	5.0	5.0	5.1
Apparent density	9.5	9.4	9.3	9.3
Tensile strength, lb./in.	24.5	23.6	21.4	22.0
Stretch, %	3.5	3.3	3.4	3.2
Tensile energy absorption, in.-lb./sq.in.	0.59	0.54	0.50	0.47
Wet tensile strength (30 min. soak), lb./in.	0.9	1.4	1.2	1.3
Ratio wet to dry tensile (30 min. soak)	0.04	0.06	0.06	0.06
Wet tensile strength (16 hr. soak), lb./in.	0.8	1.1	1.0	1.1
Ratio wet to dry tensile (16 hr. soak)	0.03	0.05	0.05	0.05

To check the possibility that additional heat treatment of the papers might bring out wet-strength characteristics, portions of the drum-dried sheets were subjected to a 30-minute heat treatment in an air circulating oven maintained at 105°C. The results of this treatment on wet-strength properties are summarized in Table II.

TABLE II

OVEN HEATING OF TREATED PAPERS

Type of polymer investigated	None	125-1	34-2	34-2
Polymer applied as wet-end additive (based on o.d. pulp), %	0	2.3	2	5
Tensile strength (drum-dried sheets), lb./in.	24.5	23.6	21.4	22.0
Wet tensile strength (30-min. soak--drum-dried sheets), lb./in.	0.9	1.4	1.2	1.3
Wet tensile strength (30-min soak--oven-treated sheets), lb./in.	1.3	1.5	1.5	1.5

It is evident that the conditions employed in these experimental failed to impart any wet strength character to the treated papers. There is insufficient material left from Mr. Snell's program for trial of other variables, but it would be possible to have additional glucose solution irradiated by High Voltage Engineering Corporation.

EXPERIMENTAL WORK WITH IRRADIATED PULPS

An auxiliary concept developed in this area was that it should be possible to irradiate cellulose pulp and, through a combination of degradation and repolymerization, arrive at a water soluble polymeric

material possibly having properties similar to Mr. Snell's irradiated glucose polymer. The experimental work conducted on this concept is described in the following paragraphs.

Preparation of Irradiated Samples

Two samples of high voltage electron irradiated pulp were processed by Frans Vaurio at the High Voltage Engineering Corporation in Rockford, Illinois. Each sample consisted of 5 8x8-inch sheets of Weyerhaeuser dry lap bleached sulfite pulp. This material was irradiated in an air-dry condition. The first sample was subjected to a treatment of 20 megarads and the second sample was given a dosage of 40 megarads.

Analysis of Irradiated Samples

Both of the irradiated samples and a portion of untreated Weyerhaeuser pulp were subjected to hot water solubility and 1% caustic solubility tests. The results are summarized in Table III.

TABLE III

SOLUBILITY CHARACTERISTICS OF IRRADIATED PULPS

Treatment	Hot Water Solubility,[a] %	One Per Cent Caustic Solubility,[b] %
None	1.5	7.0
20 megarads	3.4	26.1
40 megarads	6.0	37.5

[a]Performed according to TAPPI Method T 207 m-54

[b]Performed according to TAPPI Method T 212 m-54

The increase in pulp solubility with irradiation is a clear indication of degradation. It was hoped that the degraded products developed in this fashion would act as a wet-strength agent when they were solubilized in caustic and subsequently precipitated onto the undegraded portion of the pulp with alum.

Solubilization and Precipitation of Degraded Pulp Materials

The precipitation of caustic solubilized pulp products was briefly studied in a series of exploratory experiments. Initial solubilization of the pulp products was accomplished under approximately the same conditions utilized in the TAPPI standard method for determining 1% caustic solubility. The pulp charge, however, was increased from 2 to 8 grams, and the volume of caustic solution was increased in proportion. Detailed conditions were:

Pulp charge = 8 g. (air-dry basis) of untreated pulp
Caustic solution = 400 ml. of 1.0% caustic
Consistency of pulp in caustic solution = 2% (air-dry pulp basis)
Temperature = 95 to 97°C.
Time at temperature = one hour.

The pulp charge was dispersed in the caustic solution with a Lightnin' stirrer prior to heating, and the material was periodically stirred with the Lightnin' stirrer during the heating period.

Following the hot caustic treatment, the pulp slurry was filtered on a fritted glass crucible (porosity = 3). The undissolved portion of the pulp was discarded and the filtrate was split into two equal portions of about 200 ml. each. The first portion was then adjusted to a pH of 4.8 with a 10%

alum solution. This required 45 ml. of the alum solution, which is equivalent to about 110% alum based on the original pulp charge. Acidification of the second portion of filtrate to a pH of 4.6 with dilute sulfuric acid indicated an H_2SO_4 requirement of about 30% based on the original pulp charge. Both methods of acidification produced precipitates of the caustic soluble pulp products. Additional studies also indicated that approximately 5% alum (based on original pulp) would be required to reduce a sulfuric acid acidified filtrate from a pH of about 7 to approximately 4.5.

It was decided, on the basis of these results, that additional studies of possible wet strength development with irradiated pulps should be conducted in the following stepwise fashion.

1. Treat the irradiated pulps with hot (90 to 95°C.) 1% caustic for one hour and solubilize any products that will go into solution.
2. Precipitate the caustic soluble products in the pulp slurry by acidifying to a pH of about 7 with a 5% solution of sulfuric acid.
3. Further acidify the pulp slurry to a pH of around 4.5 with a 10% alum solution.
4. Form handsheets from the slurry at a pH of 4.5 and determine their and wet and dry strength characteristics.

The two irradiated pulp samples and portion of untreated Weyerhaeuser stock were subsequently treated in this manner. The details of these treatments are summarized in Table IV.

TABLE IV

CAUSTIC SOLUBILIZATION AND PRECIPITATION
TREATMENT OF IRRADIATED PULPS

Pulp sample	1	2	3
Irradiation dosage, megarads	0	20	40
Sample weight (air dry basis), g.	20	20	20
Volume of 1% caustic for solubilization treatment, l.	1.0	1.0	1.0
Temperature of caustic treatment, °C.	90-95	90-95	90-95
Duration of hot caustic treatment, hr.	1.0	1.0	1.0
pH of pulp slurry after caustic treatment and cooling to room temperature	12.3	12.2	12.2
H_2SO_4[a] required to reduce pH to approximately 7, (based on original air dry pulp charge), %	32	50	50
Alum[b] required to further reduce pH to 4.5-5.0 (based on original air dry pulp charge), %	4	6.5	7.0

[a]Sulfuric acid was applied as a 5% solution
[b]Alum was applied as a 10% solution

A brown color developed as soon as the irradiated samples were dispersed in 1% caustic solution. This color developed at room temperature, prior to heating, and remained throughout the subsequent heating operation and acidification treatment. In fact, a tan hue was retained in the final handsheets prepared from the irradiated samples.

Preparation and Testing of Handsheets

TAPPI standard size handsheets were formed from the acidified caustic-treated stocks, wet pressed once between blotters at 50 p.s.i., and dried on a stationary steam-heated drum drier. The sheets were then

preconditioned for at least 16 hours at 30% R.H. and 73°C., and subsequently conditioned and tested at a R.H. of 50% and a temperature of 73°F. Test results are summarized in Table V.

TABLE V

SUMMARY OF HANDSHEET TEST RESULTS
(All pulps were subjected to caustic solubilization and acidification treatments)

Irradiation dosage	None	20 megarads	40 megarads
Basis weight (25x40/500), lb.	46.8	50.8	44.7
Caliper, mils	6.7	7.1	5.7
Apparent density	7.0	7.2	7.8
Dry tensile strength, lb./in.	3.7	2.6	2.7
Wet tensile strength (0.5 hr. soak), lb./in.	0.27	0.21	0.19
Wet tensile strength (16 hr. soak), lb./in.	0.30	0.26	0.20
Stretch, %	2.4	1.4	1.3
Tensile energy absorption, in.-lb./sq. in.	0.07	0.02	0.02

It is apparent that no increase in wet strength can be attributed to the irradiated samples.

Six new samples of irradiated pulp were also received from the High Voltage Engineering Corporation. Treatment conditions for these samples are summarized in Table VI.

TABLE VI

CONDITIONS UNDER WHICH NEW SAMPLES WERE IRRADIATED WITH HIGH VOLTAGE ELECTRONS

Sample Designation	Condition of Sample During Irradiation	Irradiation Dosage, megarads
85-1	Stack of five 8 x 8-inch dry lap sheets[a] sealed in a polyethylene bag during irradiation	40
85-2		20
85-3		10
85-4		5
85-5	Stack of five 8 x 8-in. dry lap sheets[a] enclosed in manila envelope during irradiation	20
85-6		40

[a]The dry lap samples consisted of the same Weyerhaeuser bleached sulfite stock used in previous studies.

Analytical tests to determine the hot water solubility and 1% caustic solubility of Samples 85-1, 85-2, 85-5, and 85-6 are given in Table VII.

TABLE VII

WATER AND CAUSTIC SOLUBILITY OF ADDITIONAL PULP SAMPLES

Sample	Condition of Sample During Irradiation	Irradiation Dosage, megarads	Hot Water Solubility,[a] %	1% Caustic Solubility,[b] %
85-1	Stack of five 8 x 8-inch dry lap sheets sealed in polyethylene bag during irradiation	40	7.6	36.2
85-2		20	4.0	23.9
85-3		10	--	--
85-4		5	--	--
85-5	Stack of five 8x8-in. dry lap sheets enclosed in a manila envelope during irradiation	20	4.6	24.6
85-6		40	7.3	37.1

[a]Performed according to TAPPI Method 207 m-54

[b]Performed according to TAPPI Method 212 m-54

These pulps were subjected to Jokro mill prerefining and used in handsheet formation as previously described. Results are given in Table VIII.

TABLE VIII

RESULTS OF JOKRO MILL PREREFINING STUDY

Pretreatment				
Pulp sample	1	1	1	1
Irradiation dosage, megarads	0	0	20	40
Sample weight (air-dried basis), g.	20	20	20	20
Refining time in Jokro mill, min.	10	10	10	10
Caustic solubilization and precipitation	no	yes	yes	yes
Handsheet test results				
Basis wt.(25x40/500), lb.	45.9	48.1	46.6	47.8
Caliper, mils	4.5	4.8	4.3	4.8
Apparent density	10.2	10.0	10.8	10.0
Dry tensile strength, lb./in.	17.0	16.8	9.0	6.3
Wet tensile strength (0.5 hr. soak), lb./in.	0.68	0.65	0.38	0.28
Stretch	2.5	2.4	0.6	0.4
Tensile energy absorption, in.-lb/.sq.in.	0.30	0.30	0.04	0.02

The results secured in these experiments gave no indication that a polymer of the irradiated glucose type was being formed. For this reason, High Voltage Engineering Corporation was asked to subject pulps to Van de Graaff irradiation at dosages obviously degrading the pulps to the point of caramelization. Two lots of Weyerhaeuser bleached sulfite pulp were prepared and sealed in polyethylene bags. One lot had no treatment; the second was impregnated in a 1% solution of acetic acid and dried at 90°C. before sealing in polyethylene. These were irradiated under the Van de Graaff accelerator to the point of brown discoloration and loss of fiber strength. (The total dosage has not been supplied to us, but is estimated to possibly be as high as 100 megarads.)

The hot water and 1% caustic solubilities of these pulps are given in Table IX.

TABLE IX

SOLUBILITIES OF VAN DE GRAAFF IRRADIATED PULPS

Sample No.	Hot Water Solubility, %	1% Caustic Solubility, %
	Untreated Pulp	
116-I	33.6	75.0
116-II	33.0	75.0
116-III	34.3	76.2
116-IV	31.8	74.7
116-V	33.0	75.6
116-VI	31.7	75.0
116-VII	32.2	75.6
116-VIII	36.5	79.6
	Pulps Treated With Acetic Acid	
116-IX	30.8	74.0
116-XI	32.5	74.4
116-XII	29.1	69.6
116-XIII	33.0	74.4
116-XIV	31.9	74.9
116-XV	28.2	73.6
116-XVI	31.9	73.9

The high solubility figures for the Van de Graaff irradiated pulps given in Table IX confirm the heavy dosage given these materials, but there is no significant difference in solubility between the nontreated and acid-treated pulps or among the samples.

To determine whether this heavily irradiated pulp had any of the characteristics of the irradiated glucose polymer, an infrared absorption spectrum was secured for Sample 116-I in KBr. The curve obtained was quite similar to published infrared absorption spectra for cellulose II [O'Connor, Du Pré, and McCall, Anal. Chdm. 29, 999(1957)], showing none of the strong carbonyl band characteristic of Snell's irradiated glucose polymers. This not only discounts the original hypothesis that such new type polymer might be formed directly from cellulose, but also indicates that dialdehyde cellulose is not being formed in appreciable quantities. If such were found, this material might have been worthy of evaluation.

CONCLUSIONS

The conclusion reached from these experiments is that further evaluation of such irradiated materials as possible beater adhesives should await additional fundamental studies of the reaction mechanisms and products formed.